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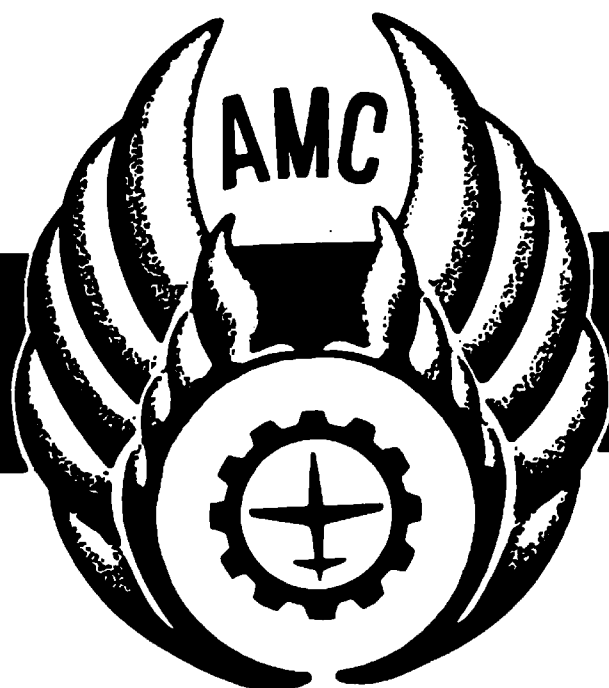
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THERMOCHEMISTRY OF PROPELLANTS

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Subject THERMO CHEMISTRY OF PROPELLANTS.

I. G. No. 0404.0700

(Brief Descriptive Title)

I.G. 804-100

From: M.A. London

Report No. R1099-46

Date 29 March 1946

Source and degree of reliability:

Armament Research Department (A.R.D.) Theoretical Research Memo 24/45.
A possible revision of Tables of Pressure-corrections in the Thermo-
chemistry of Propellant Explosions. AC8874/B.L 300. A-1

SUMMARY---Here enter careful summary of report, containing substance succinctly
stated; include important facts, names, places, dates, etc.

BRITISH SUMMARY

"In reports published in 1943, one of the authors showed how the equation of state and thermodynamic functions of propellant gases at high densities could be calculated from the forces between the molecules; these forces were themselves found from the experimental equation of state at easily-accessible temperatures. The agreement with closed-vessel results was good, the error in the predicted covolume being about five per cent. In the present report these tables are revised by using the new intermolecular field for steam, proposed by Margenau and Myers. The changes in our tables are not large, and as the error in the covolume is increased by two per cent, we do not recommend any revision of our previous results."

Al-A COMMENT: Attention is invited to the fact that various American authorities have been quoted in the attached report.

This report will be of interest to Ammunition Development Division, Ballistic Research Laboratory, and Technical Service of Picatinny Arsenal.

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Col., Ord. Dept.
Assistant Military Attache.

For the Military Attache:

Approved and Forwarded

Lt. Col., GSC,
Executive Officer.

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Ministry of Supply
Armament Research Department

THEORETICAL RESEARCH MEMO. NO. 24/45

A Possible Revision of Tables of Pressure-corrections in
the Thermochemistry of Propellant Explosions

by

J. Corner and Miss H.N. Ware

Branch for Theoretical Research,
Fort Halstead, Kent.

Copy No. 53.

26 JAN 1946

Summary

In reports published in 1943, one of the authors showed how the equation of state and thermodynamic functions of propellant gases at high densities could be calculated from the forces between the molecules; these forces were themselves found from the experimental equation of state at easily-accessible temperatures. The agreement with closed-vessel results was good, the error in the predicted covolume being about five per cent. In the present report these tables are revised by using the new intermolecular field for steam, proposed by Margenau and Myers. The changes in our tables are not large, and as the error in the covolume is increased by two per cent, we do not recommend any revision of our previous results.

Introduction

Corner (1943b) has shown how the equation of state and the thermodynamic functions of a gas under ballistic conditions can be derived from the forces between the molecules. These forces are themselves most reliably determined from the experimental equation of state at lower and more easily-accessible temperatures. When their results were compared with experimental data (Corner, 1943a), the thermodynamic tables gave results within the accuracy expected; for example, the theoretical covolume proved to be about five per cent too small.

It was explained in the reports quoted that revision of the intermolecular forces was to be expected in the future. The most likely source of changes is the highly polar molecule of steam. The only revision published in the scientific literature up to the present has, in fact, been a study of the intermolecular forces in steam, by Margenau and Myers (1944). They

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criticise the work of Stockmayer (1941) and, by implication, that of Hirschfelder, McClure and Weeks (1942) on which our steam tables were based. Margenau and Myers have developed a more complicated intermolecular potential, for which they claim better agreement with experiment and more physical plausibility. As both points are so important in the extrapolation to ballistic temperatures, we have examined the changes produced in our thermodynamic tables by the use of the newer intermolecular potential.

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TABLE I

Explosion of SC at constant volume, 300°K., density of
loading 0.2 gm./c.c.

	Earlier Tables	Present Work
T°K.	3081	3080
(CO ₂) in 10 ⁻⁵ mole/gm.	310	307
(CO) " " "	1924	1931
(H ₂ O) " " "	914	917
(H ₂) " " "	587	584
(N ₂) " " "	522	522
(OH) " " "	5	6
(H) " " "	7	7
(NO) " " "	1/2	1/2
10 ⁵ n	4274	4274
Pressure (tons/sq.in.)	17.53	17.53
Covolume (c.c./gm.)	0.96	0.94

Table I shows that the revised tables are only slightly different, and that the error in the covolume is increased by about 2 per cent.

Intermolecular potential of Margenau and Myers

This field for the water molecule can be described thus: let $V(r, \theta_1, \theta_2, \phi)$ be the potential energy of a pair of molecules whose centres of mass are at a separation r ; the line joining the centres of mass makes angles θ_1 and θ_2 with directions fixed in the molecules, and ϕ is the relative azimuth of these directions. Then if $r \ll 2.8 \text{ \AA}$,

$$V = 2.4 \times 10^{-6} \exp(-r/0.15 \text{ \AA}) - 4.5 \times 10^{-58} r^{-6} - 9.5 \times 10^{-75} r^{-8} \dots\dots\dots (1)$$

while, if $r \gg 2.8 \text{ \AA}$,

$$V = 3.25 \times 10^{-9} \exp(-r/0.28 \text{ \AA}) - 4.59 \times 10^{-59} r^{-6} - 9.5 \times 10^{-75} r^{-8} \\ - (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi) (3.52 \times 10^{-59} r^{-3} + 8.5 \times 10^{-52} r^{-5}) \dots\dots\dots (2)$$

Fundamental to our tables is the second virial coefficient B defined by

$$\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + O(V^{-3}) \dots\dots\dots (3)$$

where P , V and T are the pressure, volume and temperature of a mole of the gas.

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It can be shown that

$$B = 2\pi N \int_0^{\infty} r^2 dr \int \left\{ 1 - \exp(-V/kT) \right\} \frac{d\Omega}{\Omega}, \dots (4)$$

where $d\Omega$ is an element of the integration over the angles θ_1 , θ_2 and ϕ . Stockmayer (1941) has shown how the integral

$$\int \exp \left\{ a (2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi) \right\} d\Omega$$

can be evaluated as a power-series in a . To evaluate (4), then, it is sufficient to integrate with respect to θ_1 , θ_2 , and ϕ by this series,

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which is very rapidly convergent in the temperature range encountered in ballistics; the integration over r must be carried out numerically, using an obvious approximate integration for large r .

In this way we have computed the second virial coefficient B for steam at 700, 1600, 2000, 2400, 2800, 3200, 3600 and 4000°K.. The first value serves as a check on our working method, having been computed already by Margenau and Myers. The other values are shown in Figure 1, together with the values calculated by Corner (1943) from force-constants of Hirschfelder, McClure and Weeks (1942). The new results lie about 2 c.c./mole lower, and have a rather different temperature dependence.

In Figure 2 the second virial coefficient is plotted against T^{-1} . At higher temperatures B would show a maximum and would then fall to zero at $T^{-1} = 0$. In the region of interest here, B can be represented by the expression

$$B = 11.670 - 1.0334 \times 10^4 T^{-1} - 3.2555 \times 10^7 T^{-2} \dots (5)$$

with errors of about 0.01 c.c./mole. This was used to subtabulate B to an interval of 100°K..

The imperfection of the gas, shown by B , causes changes in its internal energy and heat content. To evaluate the relevant formulae, given by Corner (1943b), it is necessary to know dB/dT and d^2B/dT^2 as functions of temperature. These were obtained by differentiation of (5).

The third virial coefficient C , already defined in (3), is sufficiently large to be worth inclusion under ballistic conditions. As there is still no theoretical value for the third virial coefficient of a gas of polar molecules, we obtain an approximate C by the method used by Corner (1943b). The theoretical $B(T)$ was fitted to the $B(T)$ of a Lennard-Jones (12,6) potential, and the best parameters found for the latter. The $C(T)$ of a (12,6) potential has been obtained by Montroll and Mayer (1941), and hence we derive an approximate third virial coefficient for steam.

Application to S.C.

To assess the effect of the changes made, we have repeated a typical example already treated by the earlier tables. We took "S.C. at a loading density of 0.2 gm./c.c., burnt without performance of work", for which the earlier results are listed in Table I of A.R.D. Theoretical Research Report 8/43.

Table I shows the results from the two sets of tables. The differences are all small. The only result which at present can be tested against experimental data is the covolume. The observed value is 0.94 c.c./gm. at 27 tons/sq.in.; and if we allow for the trend with pressure revealed in our earlier work, we find that our results are too small by about 0.04 and 0.06 c.c./gm. respectively. Thus the change in the covolume is in the wrong direction. We do not recommend any change in our earlier tables.

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Montroll and Mayer, 1941, J. Chem. Phys. 9, 626
Stockmayer, 1941, *ibid.* 9, 398
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FIG I SECOND VIRIAL COEFFICIENTS OF STEAM FROM
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FIG II THEORETICAL SECOND VIRIAL
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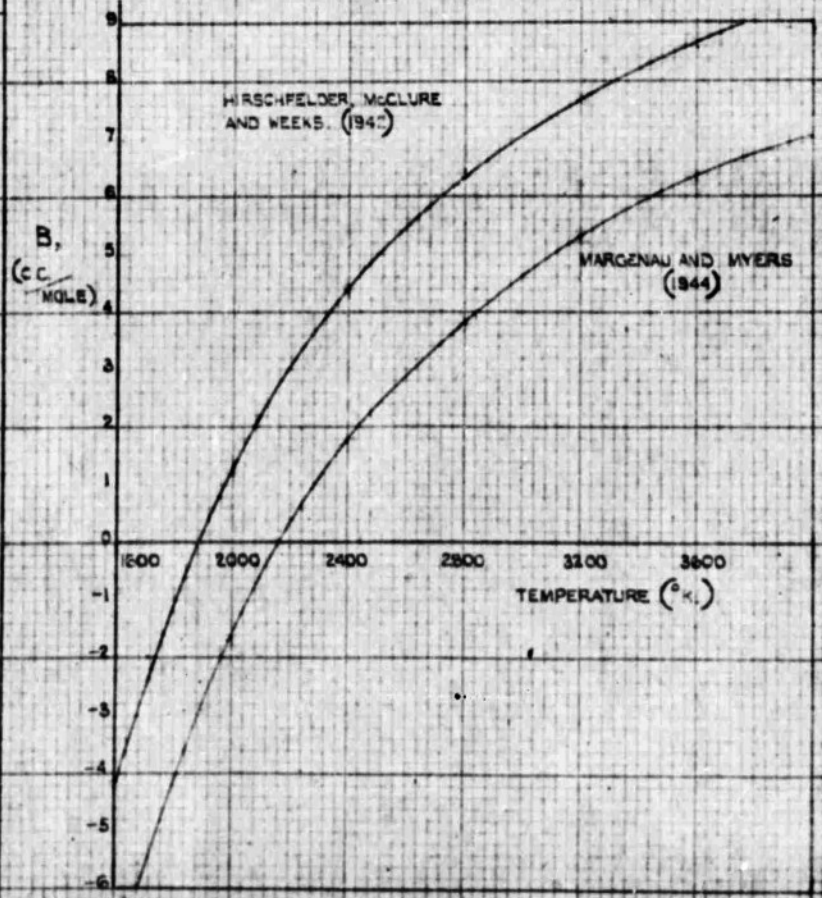


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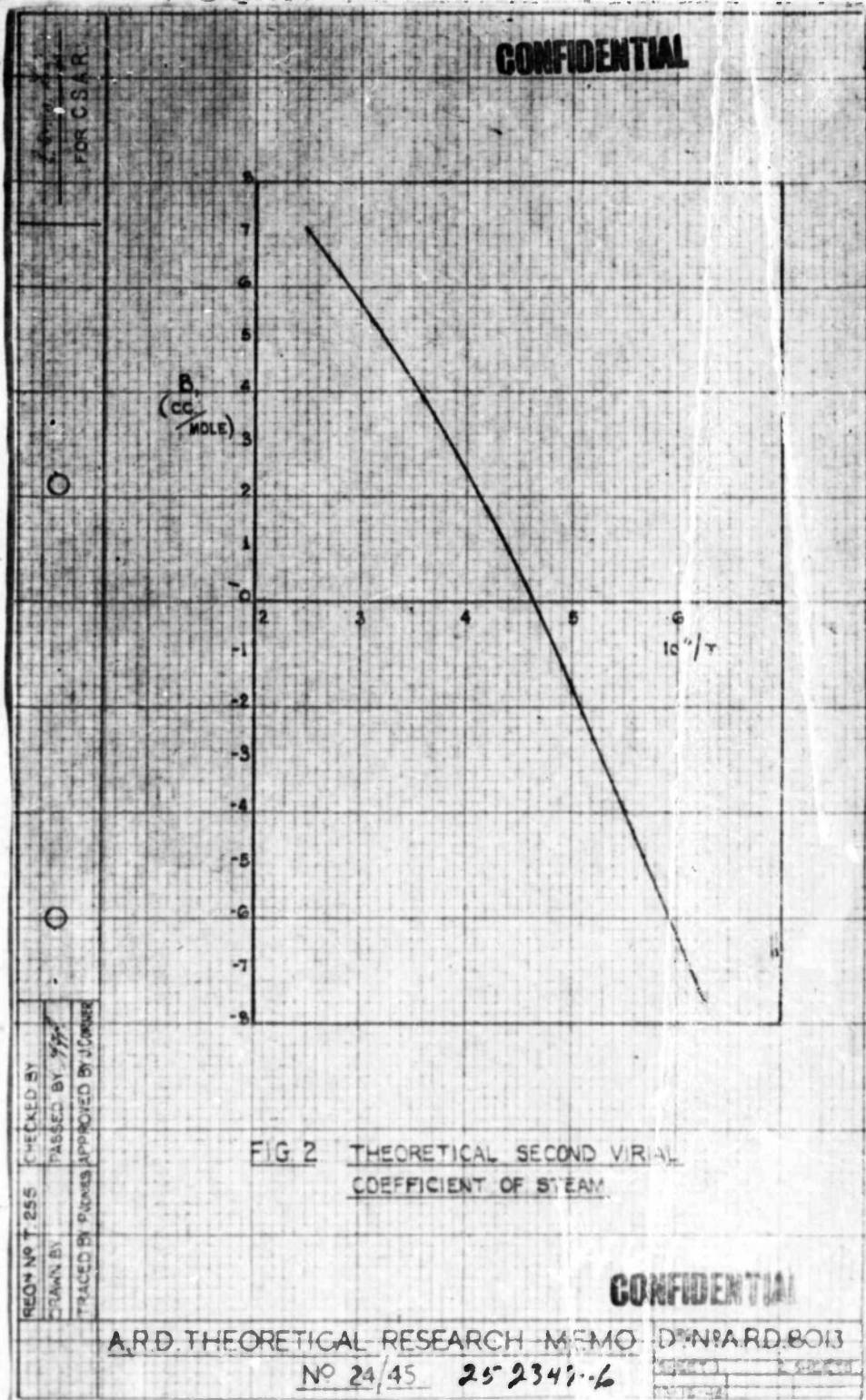
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TITLE: A Possible Revision of Tables of Pressure-Corrections in the Thermochemistry of Propellant Explosions

AUTHOR(S): Corner, J.; Ware, H. N.

ORIGINATING AGENCY: Armament Research Department, Fort Halstead, Kent

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